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SUPPORT MEMBER FOR IMAGE-RECEIVING MATERIAL IN HEAT MIGRATION TYPE THERMAL TRANSFER RECORDING

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Mitsubishi Paper Mills, Ltd. 3-4-2 Marunouchi, Chiyoda-ku, Tokyo 1. Title of the Invention

SUPPORT MEMBER FOR IMAGE-RECEIVING MATERIAL IN HEAT

MIGRATION TYPE THERMAL TRANSFER RECORDING

2. Claims

- 1. A support member for an image-receiving material in heat migration type thermal transfer recording, said support member having a base paper with natural pulp as main component and provided with a polymethylpentene resin layer on one of the image-receiving surfaces.
- 2. A support member for an image-receiving material in heat migration type thermal transfer recording according to claim 1, wherein Bekk's smoothness of said paper is 100 seconds or more.
- 3. Detailed Description of the Invention
 [Field of the Invention]

The present invention relates to a support member for an image-receiving material in heat migration type thermal transfer recording to be used in thermal transfer recording such as recording by a thermal printer, wherein heat migration type pigment such as sublimate pigment or diffusing pigment of a thermal transfer material is migrated and recording is carried out. In particular, the invention relates to a support member for an image-receiving material in heat migration type thermal transfer recording, by which high luster and high density can be

attained on the printed portion.

As an image-receiving material in heat migration type thermal transfer recording, a material has been known in the past, which has a coating layer coated with saturated polyester resin on surface of synthetic paper. Using this type of image-receiving material in thermal transfer recording, an image similar to a natural color photograph can be obtained by the following procedure: The imagereceiving material is simultaneously used with a thermal transfer material, which contains heat migration type pigment and a binder on surface of polyethylene terephthalate. These two types of materials are overlapped one upon another so that the thermal transfer layer and the image-receiving layer are brought into contact with each other. From rear surface of the thermal transfer material, heat is applied by heat-sensitive means such as a thermal head, which generates heat under control of an electric signal corresponding to an image information. The heat migration type pigment in the thermal transfer layer is transferred into the image-receiving layer, and an image similar to a natural color photograph can be produced. The heat migration type pigment referred here means a type of pigment, which can migrate from a thermal transfer material to a thermal transfer image-receiving material by a process such as sublimation or diffusion in a medium.

However, when a synthetic paper containing a resin with low heat-resistant property such as polypropylene resin is used as a support member of the image-receiving material in the heat migration type thermal transfer recording, distortion may remain on the synthetic paper due to the heat originated from heating when the image is formed, and curling may occur on the image-receiving material after the image has been formed.

When a type of synthetic paper using a resin with high heat-resistant property is employed as the support member, cushion property and heat insulating property of the support member may be low, and high printing density cannot be obtained.

To overcome these disadvantages, various attempts have been made in the past. In particular, there are strong demands to have a material with high soft-touch feeling and quality similar to that of a photograph, and many types of support members using paper as base material have been proposed as the support member for image-receiving material in heat migration type thermal transfer recording.

For instance, JP-A-62-198497 proposes a support member for image-receiving material in heat migration type thermal transfer recording, which has synthetic paper attached at least on one side of a paper substrate (hereinafter referred as "base paper"). By this proposal, improvement

was made on the curling of the image-receiving material after the formation of the image. However, smoothness of the support member is lower than the support member using only the synthetic paper, and there are problems such as transfer defect on the image. JP-A-60-236794 discloses a support member for image-receiving material in heat migration type thermal transfer recording, which has a layer of thermoplastic macromolecular substance on the base paper. However, image reproducibility is not high enough. Further, US-4,774,224 proposes the use of a support member for image-receiving material in heat migration type thermal transfer recording using a paper covered with resin having smaller value of surface roughness Ra. This proposal improved the curling of the image-receiving material after the formation of the image. However, it causes many problems such as transfer defect in the printing, insufficient printing density, thermal deformation of surface resin due to heat from a thermal head and decrease of luster on the printed portion, thereby extremely reducing the product value. Further, JP-A-1-267090 discloses a paper covered with polyethylene resin, while this has problems such as decrease of luster on the printed portion and low printing density.

[Problems to be solved by the Invention]

It is an object of the present invention to provide a

support member for image-receiving material in heat migration type thermal transfer recording, which has no problem such as curling after printing, transfer defect, etc. and can provide high luster on the printed portion without causing luster decrease due to the heat from the thermal head, and which gives superior printing density. [Means for solving the Problems]

The present inventors have been making efforts to solve the above problems and have found that the object of the present invention can be attained by a support member for heat migration type thermal transfer recording material, in which paper having natural pulp as main component is used as substrate and the other side of the image-receiving surface has polymethylpentene resin. Further, by using a base paper with Bekk's smoothness of 100 seconds or more, cumulative effects can be provided to attain the object of the present invention.

[Function]

The base paper according to the present invention uses natural pulp as main component, and pulp paper made from a mixture with synthetic pulp is used when necessary. Among these types of pulp, wood pulp such as softwood pulp, hardwood pulp, softwood-hardwood mixed pulp as main component can be advantageously used. Among natural pulp, sulfite pulp and Kraft pulp are more advantageously used.

In the base paper according to the present invention, various types of additives can be added during the preparation of paper slurry. It is advantageous to use fatty acid metal salt and/or fatty acid, alkylketene dimer emulsifier, epoxidated higher fatty acid amide, alkenyl or alkyl succinic acid dehydrate emulsifier, rosin derivative, etc. As dry paper strength reinforcing agent, anionic, cationic or ampholytic polyacrylamide or polyvinyl alcohol, cationated starch, vegetable galactomannan, etc. may be used. As wet paper strength reinforcing agent, polyamine polyamide epichlorohydrine resin may be used. As filling agent, clay, kaolin, calcium carbonate, titanium oxide, etc. may be used. As fixing agent, water-soluble aluminum salt such as aluminum chloride, conjugated sulfate, etc. may be used. As pH regulator, caustic soda, soda ash (sodium carbonate), sulfuric acid, etc. may be combined with coloring pigment, coloring dye, fluorescence whitening agent, etc. and used.

The base paper according to the present invention may contain various types of water-soluble polymer, antistatic agent or additives applied by dub-size press or by coating. As water-soluble polymers, starch type polymer, polyvinyl alcohol type polymer, gelatin type polymer, polyacrylamide type polymer, cellulose type polymer as described or disclosed in Japanese Patent Application 63-96516 may be

used. As the antistatic agents, alkali metal salt such as sodium chloride, potassium chloride, etc., alkali earth metal salt such as calcium chloride, barium chloride, etc. colloidal metal oxides such as colloidal silica, and organic antistatic agent such as polystyrene sulfonic acid salt may be used. As latex and emulsions, petroleum resin emulsion, styrene - acrylic acid - acrylic acid ester copolymer, styrene - acrylic acid - butadiene copolymer, ethylene - vinyl acetate copolymer, styrene - maleic acid acrylic acid ester copolymer, etc. may be used. As the pigments, clay, kaolin, talc, barium sulfate, titanium oxide, etc. may be used. As pH regulators, hydrochloric acid, phosphoric acid, citric acid, caustic soda, etc. combined with coloring pigment, coloring dye, fluorescence whitening agent, and other additives may be advantageously used.

As the base paper according to the present invention, it is preferable to use a type of paper with Bekk's smoothness of 100 seconds or more in accordance with JIS P 8119, or more preferably, to use the base paper with Bekk's smoothness of 200 seconds or more. When a support member having polymethylpentene resin layer is used as the base paper with Bekk's smoothness of less than 100 seconds, transfer defect is more likely to occur on the printed portion, and the density on the printed portion cannot be

kept at very high level. On the other hand, in case a support member having polymethylpentene resin layer is used on the base paper with Bekk's smoothness of 100 seconds or more, or more preferably, 200 seconds or more, no transfer defect occurs on the printed portion, and cumulative effect can be given to have higher density on the printed portion.

There are various methods to produce the base paper with Bekk's smoothness of 100 seconds or more. In general, hardwood pulp is used, which has shorter fibers and has better smoothness. This pulp is beaten by a beating machine so that long fibers can be decreased. More concretely, hardwood pulp is used by 60 weight % or more and is beaten. As the types of hardwood pulp, BSP, LBKP or LDP is more preferably used. In the beating of the pulp, it is preferable to have such pulp fiber length after beating that it contains 42-mesh component by 20 - 45% and freeness to be in the range of 200 - 350 CSF. Next, using the pulp prepared as described above, paper with uniform formation is produced by paper machine. Further, calender treatment is performed by using machine calender, supercalender, thermal calender, etc., and the base paper with Bekk's smoothness of 100 seconds or more can be prepared.

The base paper according to the present invention is generally produced by using a long-length paper machine.

There is no restriction to the thickness of the base paper.

If soft-touch feeling is taken into account, the thickness of the base paper is preferably in the range of 20 - 300 μ m, or more preferably, in the range of 30 - 250 μ m.

As the polymethylpentene resin used in the present invention, it is preferable to use 4-methylpentene-1 polymer. The resin having any value of density, melt flow rate (hereinafter referred as "MFR"), molecular weight, and molecular weight distribution may be used. Normally, the resin with density in the range of 0.820 - 0.850 g/cm³ and MFR in the range of 5 - 100 g/10 min. may be advantageously used.

To the polymethylpentene resin layer in the present invention, it is preferable to add white pigment in order to increase whiteness degree of the image-receiving material in thermal transfer recording and to improve sharpness of the image. As the white pigment, titanium oxide, zinc oxide, talc, calcium carbonate, etc. described or disclosed in JP-B-60-3130, JP-B-63-11655, JP-B-1-38291, JP-B-1-38292, JP-A-1-105245, etc. may be used. Further, the following substances may be added to the polymethylpentene resin layer: fatty acid amide such as stearic acid amide, arachidic acid amide, etc., fatty acid metal salt such as zinc stearate, calcium stearate, aluminum stearate, magnesium stearate, zinc palmitate, zinc myristate, calcium palmitate, etc., various types of

antioxidant such as hindered phenol, hindered amine, phosphorus type antioxidant, sulfur type antioxidant as described or disclosed in JP-A-1-105245, blue type pigment or dye such as cobalt blue, ultramarine blue, cerian blue, phthalocyanine blue, etc., magenta type pigment and dye such as cobalt violet, fast violet, manganese violet, etc., fluorescence whitening agent as described or disclosed in Japanese Patent Application 1-77543, or various types of additives such as UV-absorbants. It is preferable to add these additives as master patch or compound of the polymethylpentene resin.

The polymethylpentene resin layer of the support member for image-receiving material in heat migration type thermal transfer recording in the present invention can be applied to the base paper by the following methods: the so-called melt extrusion coating method to cast the heated and molten polymethylpentene resin to a running base paper; or laminating method or cladding method to apply a polymethylpentene resin film produced in advance. Prior to the application of the polymethylpentene resin layer to the base paper, it is preferable to perform activation processing such as corona discharge treatment, flame treatment, etc. to the base paper. The polymethylpentene resin layer may be processed in such manner that it has slightly rough surface or mat surface, cellular surface,

etc. as described in JP-A-55-25507. The resin layer is preferably coated with the coating material in the range of 3 - 70 g/m³, or more preferably in the range of 5 - 35 g/m³.

should should

To ensure tight adhesion between the base paper and polymethylpentene resin layer, an anchor coating layer or an adhesive layer may be provided between the base paper and the polymethylpentene resin layer. As the anchor coating agent, epoxy resin, alkyd resin, organic titanium ester compound, or ethylene - acrylic acid copolymer may be used. As the adhesive agent, the agent having vinyl acetate type emulsion, wax type hot-melt, or polyurethane type compound as main component may be used. Further, polyethylene resin layer may be provided as an easily adhesible resin layer between the base paper and the polymethylpentene resin layer. To produce multi-layer structure, it is preferable to use the so-called tandem extrusion coating system, by which two or more resin layers are produced by extrusion coating sequentially or continuously, or by the so-called co-extrusion coating system, by which two or more resin layers are coated by extrusion coating at the same time. As the polyethylene resin, low density polyethylene, moderate density polyethylene, high density polyethylene, straight-chain low density polyethylene, copolymer of ethylene and propylene, carboxylic denatured polyethylene, etc. or mixture of these substances may be used. The compound with any value of density, MFR, molecular weight, and molecular weight distribution may be used, while it is advantageous to use the compound with density in the range of 0.90 - 0.97 g/cm³ and with MFR in the range of 1 - 30 g/10 min. It is preferable to promote the contact between the anchor coating layer, the adhesive layer, or the polyethylene resin layer and the base paper by activation treatment such as corona discharge on the base paper.

On the other side (rear side) of the base paper of the present invention opposite to the resin layer side (front side) where the image-receiving layer of heat migration type thermal transfer recording is provided, a resin layer having film forming potency may be applied to provide curling preventive effect, paper feeding property, and antistatic property to the image-receiving material. As this resin, any type of resin film may be used, which can cover the base paper, and there is no special restriction, while it is preferable to use thermoplastic resin such as polyethylene resin, polystyrene, polymethylpentene, polypropylene, polyethylene terephthalate, polycarbonate, The surface of the resin layer is normally lusterless, and the surface of the base paper is preferably processed by corona discharge prior to the application of the resin layer. Coating amount of the resin layer on the rear side

of the base paper may be set in an adequate range to keep balance with the resin layer on the front side.

As the synthetic resin used in the image-receiving layer of heat migration type thermal transfer recording according to the present invention, the following resin may be used: resin having ester bonding such as polyester resin, polyacrylic acid ester resin, polycarbonate resin, polyvinyl acetate resin, styrene acrylate resin, vinyl toluene acrylate resin, etc.; resin having urethane bonding such as polyurethane resin; resin having amide bonding such as polyamide resin; resin having urea bonding such as urea resin, or other resin such as polycaprolactam resin, styrene type resin, polyvinyl chloride resin, vinyl chloride - vinyl acetate copolymer resin, polyacrylonitrile resin, etc. In addition to these types of resin, mixture of these resins or copolymer of these resins may be used.

In the image-receiving layer of heat migration type thermal transfer recording according to the present invention, mold release agent, pigment, etc. may be added in addition to the synthetic resin as described above. As the mold release agent, the following substance may be used: solid waxes such as polyethylene wax, amide wax, Teflon powder, etc., fluorine type or phosphoric acid ester type surface active agent, or silicone oil. Among these types of mold release agents, silicone oil is most

preferably used. As the silicone oil, oily substance may be used while it is preferable to use curing type oil. As the curing type silicone oil, reactive curing type, photosetting type, catalytic curing type silicone oil, etc. may be used, while it is most preferable to use the reactive curing type silicone oil. As the reactive curing type silicone oil, amino denatured silicone oil, epoxy denatured silicone oil, etc. may be used. It is preferable to add the above reactive curing type silicone oil in an amount of 0.1-20 weight % in the image-receiving layer. As the pigment, it is preferable to use extender pigment such as silica, calcium carbonate, titanium oxide, zinc oxide, etc. The thickness of the image-receiving layer is preferably in the range of $0.5-20~\mu\text{m}$, or more preferably, in the range of $2-10~\mu\text{m}$.

[Embodiments]

Detailed description will be given below on the present invention referring to embodiments, while the scope of the present invention are not limited to these embodiments.

(Example 1)

Using a mixture for paper-making as given below, base paper was produced under the predetermined paper-making conditions. The paper-making conditions included: mixing ratio of the pulp used, beating conditions such as average

fiber length after beating and freeness, coating amount of ethylene - acrylic acid copolymer and carboxylic denatured polyvinyl alcohol, linear pressure of calendar, etc. As a result, a base paper with Bekk's smoothness as given in Table 1 was obtained.

Mixed pulp containing hardwood bleached sulfite pulp and hardwood bleached Kraft pulp was beaten. Further, to 100 weight parts of pulp, 3 weight parts of cationated starch, 0.2 weight part of anionated polyacrylamide, 0.4 weight part of alkyl ketene dimer emulsifier (as ketene dimer component), and 0.4 weight part of polyaminopolyamide epichlorohydrine resin were added, and paper with basis weight of 160 g/m3 was produced. Wet paper thus produced was dried at 110°C. Then, a coating solution (containing ethylene - acrylic acid copolymer, carboxylic denatured polyvinyl alcohol, fluorescence whitening agent, blue dye, citric acid and water) was coated at a rate of 25 g/m². This was dried under hot air of 110°C and was treated by super-calender processing. Then, both surfaces were processed by corona discharge, and a base paper for support member of image-receiving material in heat migration type thermal transfer recording was produced.

Next, a resin composition (containing 20 weight parts of master patch of titanium dioxide pigment and 80 weight parts of polymethylpentene resin (density 0.835 g/cm³, MFR

26 g/10 min.)) was coated on the surface of the base paper by melting extrusion at resin temperature of 305°C to have a thickness of 13 μ m. The above master patch contained polymethylpentene resin by 47.5 weight % (density 0.835) g/cm³, MFR 26 g/10 min.), anatase type titanium pigment by 50 weight % processed by surface treat treatment using aluminum oxide hydrate (0.75 weight % as Al₂O₃ component to titanium dioxide), and zinc stearate by 2.5 weight %. For comparison purpose, a specimen was also prepared, which contained low density polyethylene resin (density 0.920 q/cm³, MFR 4.5 q/10 min.) or polypropylene resin (density 0.910 q/cm³, MFR 40 g/10 min.) instead of polymethylpentene resin. Also, prior to the coating of a resin layer on the surface of the base paper, a resin composition containing 80 weight parts of high density polyethylene resin (density 0.350 q/cm3; MFR 30 q/10 min.) and 20 weight parts of low density polyethylene resin (density 0.920 g/cm3; MFR 1.5 g/10 min.) was coated on opposite side (rear surface) of the base paper at resin temperature of 310°C by melting extrusion to have the same thickness as the layer on the front surface. In this case, the surface of the resin layer containing titanium dioxide pigment of the support member for image receiving material in heat migration type thermal transfer recording was fabricated in such manner that it was to have a very flat glossy surface on the front surface and a mat surface just like paper on the resin layer of the rear surface.

Then, corona discharge was performed on the surface. An image-receiving layer of the composition given below was coated on the surface by using a wire bar, and this was dried. An image receiving layer with solid matter coating amount of 5 g/m^3 was provided, and an image-receiving material for heat migration type thermal transfer recording was prepared.

Composition for forming the image receiving layer:

Saturated polyester resin 10 weight parts

Amino denatured silicone 0.5 weight part

Solvent (xylene/methyl ethyl ketone = 1/1)

30 weight parts

Next, an ink composition for forming the heat migration type thermal transfer layer with the composition as given below was prepared. On a polyethylene terephthalate film with thickness of 6 μ m processed by heat-resistant treatment on rear surface, the ink composition was coated to have solid matter coating amount of 1 g/m³ and this was dried, and a material for thermal transfer was prepared.

Heat migration type pigment

(C.I Solvent Blue 95) 5 weight parts
Polysulfonic resin 10 weight parts

Chlorobenzene

85 weight parts

The thermal transfer material and the image-receiving material for thermal transfer recording prepared as described above were combined together. By applying energy via thermal head, allover printing was carried out. Then, density of the printed portion was measured by using Macbeth densitometer. Also, degree of decreased luster on the printed portion, transfer defect, and density unevenness on the printed portion were judged by visual inspection. The application energy on the specimen for density measurement was adjusted in such extent that luster decrease did not occur almost at all on the printed portion of the comparative specimen. The results thus obtained are summarized in the table below.

	Resin type of surface resin layer	Bekk's smoothness of base paper (sec.)	Density	Degree of luster decrease (Note 1)	Transfer defect and density unevenness on the printed portion (Note 2)
The present invention	Polymethyl pentene	70 100 200 400	1.35 1.50 1.70 1.75	© © ©	Δ Ο Θ Θ
Comparative specimens	Polyethylene	70 100 200 400	1.25 1.35 1.45 1.45	Δ Δ Δ	х Δ О
	Poly- propylene	70 100 200 400	1.30 1.40 1.55 1.60	0Δ 0Δ 0Δ	х Δ О

(Note 1) Criteria for evaluation were as follows:

1 No decrease of luster. Luster extremely high.

 $O\Delta$: Luster slightly decreased. Luster somewhat low.

 Δ : Luster somewhat decreased. Luster was low.

(Note 2) Criteria for evaluation were as follows:

O: Transfer defect and density unevenness not found almost at all.

O: Transfer defect and density unevenness slightly recognized.

 Δ : Transfer defect and density unevenness recognized to some extent, but the specimen was suitable for practical use.

X: Transfer defect and density unevenness recognized.
There are problems for practical use.

As it is apparent from the above, when the base paper has polymethylpentene resin layer on the image-receiving surface, there was no problem such as transfer defect, density unevenness and luster decrease on the printed portion. It was suitable as a support member for image-receiving material in heat migration type thermal transfer recording. When the base paper had Bekk's smoothness of 100 seconds or more, or more preferably, 200 seconds or more, printing density was very high, and it was a support member with superior quality for practical use.

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(Example 2)

Specimens of base paper were prepared under the same conditions as in Example 1 except that coating amount of the resin on the surface (containing titanium dioxide pigment) was 13 g/m^3 , 25 g/m^3 , 35 g/m^3 and 60 g/m^3 respectively, and the coating amount of the resin on the opposite side of each specimen was set to the same thickness as on the front side.

As a result, with the increase in the coating amount of the resin on the front surface side, printing density substantially did not decrease in the specimen according to the present invention, which uses polymethylpentene resin, and an image was obtained, which had neither transfer defect nor density unevenness and showing quality similar to a photograph. In the specimens not based on the present invention using polyethylene resin or polypropylene resin, there were problems such as the decrease of printing density.

[Effects of the Invention]

According to the present invention, it is possible to provide a support member for the material in heat migration type thermal transfer recording, in which no density unevenness is found and no luster decrease occurs on the printed portion, and which shows high quality similar to that of a photograph with high printing density.